ATERBIO – ENVIRONMENT FRIENDLY FUNCTIONAL BARRIER TEXTILES BASED ON PHOTOACTIVE PHTHALOCYANINE DYEINGS

L. Martinková[1], R. Kořínková[2], M. Karásková[2], M. Vrtalová[3], V. Špelina[3]

[1]INOTEX, spol. s r.o., Štefánikova 1208, 544 01 Dvůr Králové n. L., Czech Republic, martinkova@inotex.cz
[2]Centre for Organic Chemistry, Ltd, Pardubice, Czech Republic
[3]National Institute of Public Health, Prague, Czech Republic

Abstract: *An innovative photoactive phthalocyanine based antimicrobial system used for textile barrier finishing was studied and optimized as a new tool for photo-initiated antimicrobial functionality of textiles. A range of photoactive phthalocyanines containing Zn or Al and reactive groups capable to create a covalent bind with cellulosic fibres was synthesised and applied on the cotton fabric by the reactive dyeing process. The antimicrobial efficiency of the finished fabrics was determined according to a modified standard relevant for health-care textiles evaluation during repeated washing and chemo-thermo-disinfection maintenance cycles. The unique properties of textiles dyed with photoactive phthalocyanine derivatives were confirmed. This type of textile finishing can be used for simultaneous dyeing and preparation of antimicrobial/self-cleaning textile materials with a long-lasting wash-permanent barrier effect as an effective, safe and less environmentally risky alternative of conventional antimicrobial systems.*
Key Words: *textile finishing, photocatalysis, phthalocyanines, reactive dyeing, antimicrobial activity*

1 INTRODUCTION

Photoactivity of phthalocyanine compounds (PTCs, Fig. 1). containing certain metals as a central atom is based on production of singlet oxygen $^1O_2$ when exposed to light This highly reactive form of oxygen is able to kill majority of microorganisms and to destroy some pollutants. The lifetime of the singlet oxygen is only several microseconds and therefore the field of its effect is up to 20 nm distance from a surface modified by these PTC derivatives. These unique properties of photoactive PTCs were used for preparation of antimicrobial/self-cleaning textile materials with long-lasting wash-permanent barrier effect as an effective and safe alternative of conventional antimicrobial systems because firmly fixed on textile fibre [1, 2].

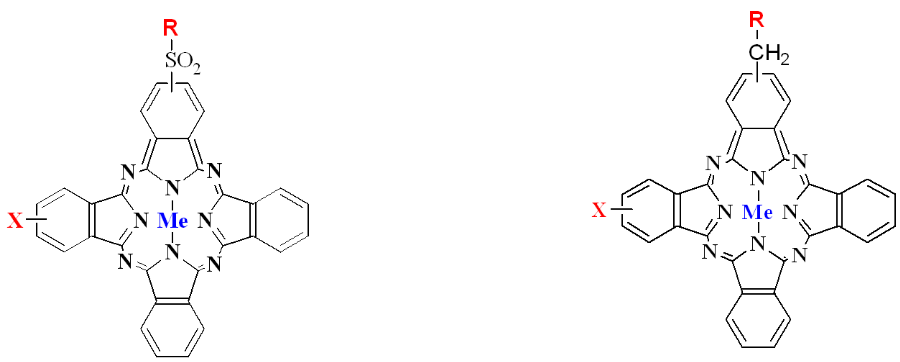

Figure 1 General structure of synthesised phthalocyanines (Me=metal, R=reactive group/s, X=solubilising group/s)

A range of PTCs containing Zn or Al in their structure and reactive groups capable to create a covalent bond with the cellulosic fibre was synthesised in Centre for Organic Chemistry, Pardubice. These derivatives were applied on cotton fabric in INOTEX, Dvůr Králové n. L. as reactive dyestuffs under optimized conditions. Resulting colourfastnesses were evaluated according to relevant standards. Testing of photoactivity of the finished textiles was conducted in Centre for Organic Chemistry by means of an iodide method. Antimicrobial activity of the finished textiles was evaluated in the National Institute of Public Health, Prague according to the modified standard EN ISO 20743 after dyeing and repeated maintenance cycles (washing at 60 °C and chemo-thermo-disinfection) conducted in the Commercial Laundry & Dry Cleaning Company (Náchod, Czech Republic).

2 EXPERIMENTAL

Photoactive PTCs

14 greenish derivatives of photoactive PTCs containing Zn or Al as a central metal atom and reactive vinylsulfone (VS) or monochlorotriazine (MCT) groups typical for reactive dyestuffs were synthesised and prepared in a purified powder form ready for dyeing process.

Reactive dyeing – antimicrobial finishing

The reactive PTC derivatives were applied on a cotton fabric (100% cotton CARLTON -Mileta a.s. CZ, plain weave, square weight 120 g/m^2, pretreated and prebleached for dyeing), as reactive dyes using a conventional exhaustion process on Labomat dyeing lab device at a liquor ratio 1:10 (Fig. 2):

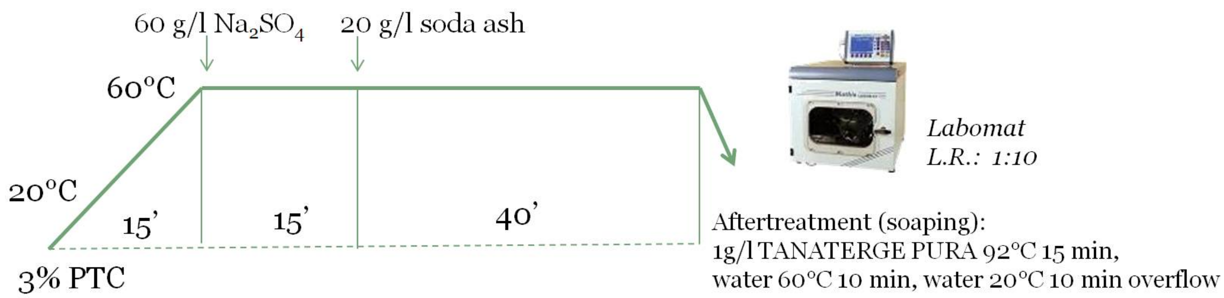

Figure 2: Reactive dyeing scheme

Evaluation of photoactivity of PTC dyed fabrics

Testing of photoactivity of the finished textiles is based on evaluation of their capability to produce singlet oxygen. These tests were performed using an iodide method determining a rate of triodide production at the presence of the singlet oxygen (Eq.1). The triodide content growth was observed spectrophotometrically (absorption at λ=351 nm). The photocatalytic effect of the fabrics was necessary to be initiated: a LED light source emitting a red radiation suitable for PTCs excitation under defined conditions was used (Fig. 4).

$$\boxed{\begin{array}{l} {}^{1}O_2 + 2I^- \xrightarrow{H^+} I_2 \\ I_2 + I^- \longrightarrow I_3^- \end{array}}$$

Equation 1: Triodide forming at single oxygen presence

Figure 4: Testing of photocatalytic activity of fabrics

Antimicrobial activity of PTCs dyed fabrics

Textiles finished (dyed) with the PTC derivatives (1146/75 – Zn/VS and PTC 1134/231- Al/VS) with the best synthesis reproducibility and colouration/photoactive properties were proceeded to microbiological testing performed in the National Institute of Public Health, Prague. The antimicrobial effect and its permanency were evaluated also after repeated washing (60 °C) and chemo-thermo-disinfection cycles as a prescribed maintenance procedure for fabric used in health-care sector. For the antimicrobial efficiency testing according to the modified quantitative standard EN ISO 20743 following bacteria strains were used: G-negative *Escherichia coli,* CCM 4517 and G-positive *Staphylococcus aureus,* CCM 4516).

The microbiological tests were conducted under intensity of light radiation 2,1 and 5 J/cm^{-2} necessary for photocatalytic effect initiation. As light sources two following different artificial light-sources necessary for the PTC photoactivation were selected:

- *Energy Saving SPIRAX SP0318 MEGAMAN, E 27, 18 W, 1200 lm 2700 K (warm white):* a lamp with a wavelength simulating light conditions in building interiors with a limited daylight access
- *NARVA LT 36 W/D65, artificial daylight, COLOURLUX proof*, and a lamp-tube simulating outdoor daylight environment. UV parts of spectra were eliminated in both lamps.

The evaluation of antimicrobial activity of textiles according to the standard EN ISO 20743 were performed using the standardized Absorption method (an evaluation method in which the test bacterial suspension is inoculated directly onto samples) in Petri dishes (contact time 18 – 24 h, temperature 37° C). Antibacterial activity (A) was calculated according to Eq. 2:

$$\boxed{A = (\log C_t - \log C_0) - (\log T_t - \log T_0) = F - G}$$

Equation 2

where $F = C_t - C_0 =$ Growth value on the control sample (untreated)
$G = T_t - T_0 =$ Growth value on the antibacterial sample (PTC finished)

3 RESULTS AND DISCUSSION

Reactive dyeing - colourfastnesses

Resulting colourfastnesses were evaluated in INOTEX accredited lab according to relevant standards. The best fastnesses results and also good synthesis reproducibility were obtained at two VS reactive group-containing PTC derivatives (Zn containing PTC 1164/75 and Al containing PTC 1134/213 – Fig. 3):

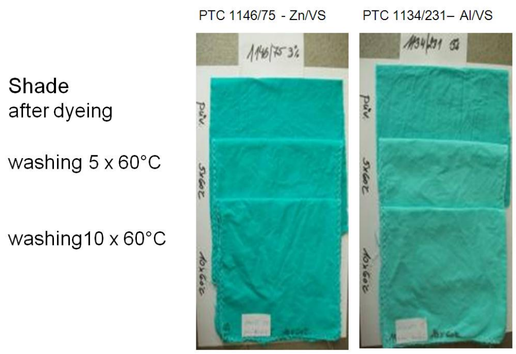

Figure 3: Phthalocyanine dyed cotton fabric (PTC 1146/75 – Zn/VS and PTC 1134/231- Al/VS)

Colourfastnesses of these two reactive dyeings are summarized in Table 1:

Table 1: Colourfastnesses of selected PTC dyed cotton fabrics

Colourfastness	**Standard**	**PTC 1164/75 – Zn/VS**	**PTC 1134/231 – Al/VS**
in water	EN ISO 105-E01	4-5/4/4	4-5/4/4
in alkaline perspiration	EN ISO 105-E04	4-5/3-4/3-4	4-5/3-4/4
in acid perspiration	EN ISO 105-E04	4/4-5/4-5	4-5/4/4
in washing 60°C (C1S)	EN ISO 105-C06	3-4/3/3-7	3/3-4/4
rubfasness - wet	EN ISO 105-X12	4-5 warp	4-5 warp
rubfastness - dry	EN ISO 105-X12	4 warp	4-5 warp
lightfastness	Q-SUN XE1S*	3-4D	3-4D

*60 W/m^2, 16 hrs

Values of colourfastnesses in Table 1 are usual for reactive dyeing with PTC –based dyestuffs and textile with these colouration properties are acceptable for using in health-care sector.

Photoactivity of PTC dyed textiles

The photoactivity of fabric as a singlet oxygen production can be expressed as a direction k_{obs} of the linear dependency A (531 nm) = f(t). The results o photoactivity after dyeing and after repeated washings are demonstrated in Table 2. The washing of textiles was conduced under standardized conditions according to EN ISO 6330 (Wascator) at 60°C (process 6N).

Table 2: Photoactivity of finished and dyed fabrics as a singlet oxygen production (k_{poz})

Sample (PTC)	k_{obs} .10^2 [min^{-1}]		
	unwashed fabric	washed 5 x 60°C	washed 10 x 60°C
PTC 1164/75 – Zn/VS	3,23	5,92	5,92
PTC 1134/231 – Al/VS	14,00	22,36	23,71

From these results it is obvious that even after 10 washings the both fabrics produce the singlet oxygen necessary for inhibition of microorganisms. The lower values at unwashed samples (repeatedly found) can be explained probably by the presence of a trace amount of an unspecified scavenger of triplet state of the PTCs. The speed of production of the singlet oxygen is higher at Al-containing PTC sample compared with Zn-PTC. The photoactivity of the dyed cotton textiles is obviously high and stable in repeated washing cycles. Lower grow rates observed at the unwashed samples are probably caused by the presence of traces of some excited PTCs extinguishers.

Antimicrobial activity of PTC dyed fabrics

Results of the antimicrobial activity of PTC dyed textiles under indoor and outdoor light conditions (under two different light intensity) after finishing and repeated washings are summarized in Tab.3. Results of antimicrobial activity of textiles under indoor light conditions after finishing, repeated washing and chemo-thermo-disinfection cycles are summarized in Tab. 4.

Table 3: Antibacterial activity of PTC dyed cotton fabric after finishing and repeated washing

Antibacterial activity – A (log)					
	Cotton fabric dyed with PTC 1146/75 (3% dyeing)	**Light source**	**Light exposition (J/cm^{-2})**	***S. aureus***	***E. coli***
1)	Unwashed	daylight indoor conditions SPIRAX	2,1	5,1	6,5
	5 x washed at 60°C			1,9	2,9
	10x washed at 60°C			1,2	2,3
2)	Unwashed	daylight outdoor conditions NARVA	5,0	4,6	5,1
			2,1	4,7	3,8
	5 x washed at 60°C		5,0	4,7	5,0
			2,1	4,6	3,8
	10x washed at 60°C		5,0	4,6	5,0
			2,1	4,8	3,7

Table 4: Antibacterial activity of PTC dyed cotton fabric after finishing and repeated washing and chemo-thermo-disinfection cycles (light source: SPIRAX, light exposition: 2,1 J/cm^{-2})

Antibacterial activity – A (log)			
Maintenance cycles	**Cotton fabric dyed with PTC 1134/231 (3% dyeing)**	***S. aureus***	***E. coli***
Washing	Unwashed	5,5	4,9
	5 x washed at 60°C	5,6	4,1
	10x washed at 60°C	3,0	3,5
Washing + Chemo-tremo-disinfection	Unwashed	5,0	6,0
	5 x washed at 60°C + CHT	5,0	5,5
	10x washed at 60°C + CHT	5,0	5,4

From results in Tab. 3 and 4 it is obvious that photo-induced antimicrobial activity of PTC dyed cotton fabric (derivative PTC 1146/75 – Zn/VS) is high and reliable against both G+ and G- bacterial strains even after repeated washing and thermo-disinfection cycles under indoor and outdoor light conditions.

4 CONCLUSIONS

Photoactive PTC derivatives applicable as a functional reactive dyes for cotton antimicrobial finishing were successfully synthesized and. Their application by the conventional exhaustion dyeing process resulting in good colourfastnesses was verified and optimized. The photoactivity of PTC finished textiles was identified and evaluated after dyeing and repeated washing.
From the results of antibacterial activity it can be concluded that cotton fabric dyed with a photosensitive PTC derivative shows a high antimicrobial effect against both G+ and G- bacteria strains. This effect is stable in repeated washings at 60° C. Moreover the stability of the effect in repeated washing followed by a chemo-thermo-disinfection prescribes for textiles maintenance processing in the health care sector has been proved. This barrier finishing/dyeing technology has been up-scaled and verified by semi-industrial trials and is now ready to be transferred to the industrial scale. It represents an effective non-toxic and eco-friendly alternative of antimicrobial finishing systems and is suitable for apparel textiles and bed-linens.

Acknowledgement: *The work was supported by the Technology Agency of the Czech Republic – project of Competence Centres TE02000006 ALTERBIO – Centre for alternative friendly high effective polymer antimicrobial agents for industrial applications.*

5 REFERENCES

1. Graf, Gregor; Hoelzle, Gerd; Reinert, Gerhard: „Water-soluble pthalocyanine compounds and their use as photoactivators“- From Eur. Pat. Appl. (1985), EP 153278 A2 19850828
2. Hoelzle, Gerd; Reinert, Gerhard; Polony, Rudolf: „Bleaching textiles and controlling microorganisms” - From Eur. Pat. Appl. (1982), EP 47716 A2 19820317